

JP 40412302 A
JUN 1992

09-525,176

(54) PRODUCTION OF HYDROGEN

(11) 4-182302 (A) (43) 29.6.1992 (19) JP

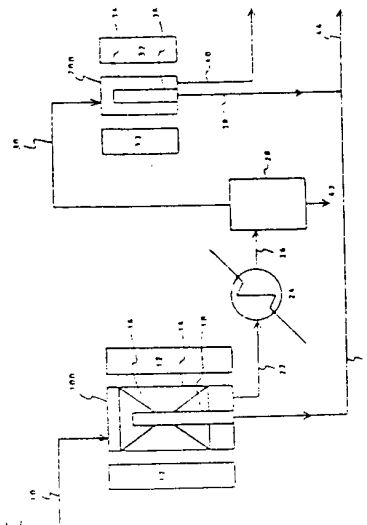
(21) Appl. No. 2-310577 (22) 15.11.1990

(71) SEKIYU SANGIYOU KATSUSEIKA SENTAA(1) (72) SHIGEO HIYAMA(1)

(51) Int. Cl.⁵ C01B3/38, B01D53/22, C01B3/56

PURPOSE: To improve the recovery rate of hydrogen by diffusing the hydrogen in the gas produced by the steam reforming reaction through a first membrane, cooling the unpassable gas remaining in a reactor to condense and separate steam, and then diffusing the remaining hydrogen through a second membrane.

CONSTITUTION: The gaseous mixture of hydrocarbons and steam is introduced into a reactor 100 packed with a steam reforming catalyst 16 between a first hydrogen permselective membrane 18 and an outer vessel 14 through a duct 10, heated to 300-700°C by a heater 12 and catalyzed, and the hydrogen in the product gas is partly diffused through the membrane 18 and discharged from a duct 20. Meanwhile, the unpassable gas remaining in the reactor 100 and contg. hydrogen and steam is introduced into a cooler 24 to condense steam, which is discharged from a gas-liquid separator 28 as condensed water 42. The remaining product gas is introduced into a membrane separator 200 heat-insulated by a heater 32, and the hydrogen is diffused through a second hydrogen permselective membrane 36 and discharged from a duct 38.



⑨ 日本国特許庁(JP)

⑩ 特許出願公開

⑫ 公開特許公報(A)

平4-182302

⑮ Int. Cl.⁵

識別記号

庁内整理番号

⑬ 公開 平成4年(1992)6月29日

C 01 B 3/38
B 01 D 53/22
C 01 B 3/56

A

9041-4G
8822-4D
9041-4G

審査請求 未請求 請求項の数 1 (全6頁)

⑭ 発明の名称 水素の製造方法

⑯ 特 願 平2-310577

⑰ 出 願 平2(1990)11月15日

⑱ 発 明 者 飯 山 繁 生 千葉県茂原市高師151-14

⑲ 発 明 者 堺 直 人 千葉県千葉市高洲2-6-12-209

⑳ 出 願 人 財団法人石油産業活性化センター 東京都港区麻布台2丁目3番22号

㉑ 出 願 人 東洋エンジニアリング株式会社 東京都千代田区霞が関3丁目2番5号

㉒ 代 理 人 弁理士 古 谷 馨 外3名

明 細 書

1. 発明の名称

水素の製造方法

2. 特許請求の範囲

- 1 壁の1部を水素選択透過性の第1の膜で形成し、且つ水蒸気改質触媒を内蔵した反応器に炭化水素及び水蒸気を導入して300~700℃で接触反応させ、同時に反応生成ガス中の水素を該第1の膜を透過させて分離し、反応器に残存した水素及び水蒸気を含む非透過ガスを取り出し冷却して水蒸気を凝縮分離させた後、このガスから水素を水素選択透過性の第2の膜で分離することを特徴とする水素の製造方法。

3. 発明の詳細な説明

(産業上の利用分野)

本発明はナフサ、天然ガス、LPG、都市ガス等の炭化水素を主成分とする原料を水蒸気改質して水素を製造する方法に関するものであり、特に半導体エピタキシャル用及びシリコン単結

晶用等のIC用途に用いる純度が99.99%以上の高純度水素にも適する製造方法に関する。

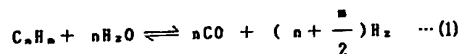
(従来の技術及びその課題)

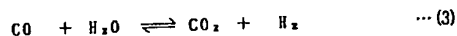
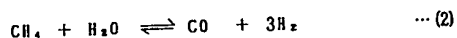
ナフサ、天然ガス、LPG等より水蒸気改質反応を利用して水素を製造する方法は工業的に広く用いられている。

この方法は、改質器に原料の炭化水素と水蒸気を連続的に供給し、700~900℃に加熱された触媒層において、次式に示すような水蒸気改質反応により、 H_2 、 CO 、 CO_2 、 CH_4 、 H_2O の混合ガスを製造するものである。この混合ガスは更にCO変成器、脱炭酸装置、メタン化装置により分離・精製されて水素ガスが製造される。

分離・精製法として上記混合ガスを冷却し、水蒸気を凝縮分離後、水素選択透過性膜により水素を透過させて分離採取する方法も公知である。

炭化水素の水蒸気改質反応は一般に次の(1)~(3)式に従う。





(2), (3)の反応は可逆的であり、この熱力学的平衡より、水素の多いガスを製造するためには高温の条件が必要である。この方法では次のような問題点を有している。

- ① (2), (3)式の反応(以下水素生成反応という)が可逆的であるため、改質ガスは H_2 , CO , CO_2 , CH_4 , H_2O の混合ガスとなる。従って、純度の高い H_2 ガスを製造するためには、改質ガスを一旦、系外に取り出し、分離、精製により H_2 ガスを製造する必要がある。即ち、改質器のほかに分離・精製装置を設ける必要があり、工程が複雑となる。
- ② (2), (3)の水素生成反応率を向上させるため反応温度を $700^\circ\text{C} \sim 900^\circ\text{C}$ としあるいは水蒸気/炭化水素比を高くする必要がある。しかし、水素生成反応の可逆性から熱力学平衡値を越える転化率は不可能である。
- ③ 装置全体が大型化すると共に、加熱用燃料

を多く必要とする。

- ④ 水蒸気改質用触媒は $700 \sim 900^\circ\text{C}$ の耐熱性が要求される。

以上のように、上記技術では高温反応($700 \sim 900^\circ\text{C}$)を起こさせるため、改質器が大型化し、かつ材料の耐熱性も必要である。また、エネルギーコストが増大する。

上記技術の問題点を解決する方法として、壁の1部を水素選択透過性膜で形成し、かつ水蒸気改質触媒を内蔵した反応器に炭化水素及び水蒸気を導入して接触反応させ、同時に反応生成ガス中の水素を該水素選択透過性膜を透過させて分離採取する水素製造方法が知られている(特開平1-219001号公報)。

この方法によれば、反応と同時に生成水素を反応系外に除去するため、上記(1)~(3)式で示す平衡が生成側に移動し、

- ① 水素収率が熱力学的平衡値よりも増大する、
② 反応温度を低下させることができる、
③ 反応後の分離・精製操作の省略が可能とな

る、

- ④ これらを通して省エネルギープロセスが実現する等の長所を持っている。

しかしながら、この方法は次に記すような欠点を持っている。

- ① 一般に水素の膜分離の場合、膜非透過側水素分圧と膜透過側水素分圧の差が大きくなるほど水素透過量が增大するが、炭化水素の水蒸気改質反応生成ガス中には通常水蒸気が $20 \sim 60 \text{ Vol}\%$ 残存し、水蒸気の存在しない場合に比較してこのぶん膜非透過側水素分圧が小さく、膜透過側の水素分圧との差が小さくなり、水素の膜透過による回収率(生成水素量に対する透過水素の比率)に限界がある。

水蒸気改質反応生成ガス中の水蒸気残存量を減少させるために、反応器に供給する水蒸気と原料炭化水素のモル比を小さくすることも考えられるが、このようにすると改質触媒上に炭素が析出し易くなり、触媒寿命が低下するため、改質反応生成ガス中の残存水蒸気

をなくすことは実用上不可能である。

- ② 水蒸気改質反応生成ガス中の膜非透過側水素分圧と膜透過側の水素分圧の差を大きくするために透過ガス側をアルゴンガス等の不活性ガスでバージし、透過側の水素分圧を低下させる方法が知られているが、この場合、製品水素中にアルゴンガス等が混合し、不純物濃度を高める原因となる。

本発明は炭化水素を主成分とする原料の水蒸気改質による水素の製造において前記従来技術に比較し、高い水素回収率を与える水素の製造方法を提供することを目的とする。

(課題を解決するための手段)

即ち本発明は、壁の1部を水素選択透過性の第1の膜で形成し、且つ水蒸気改質触媒を内蔵した反応器に炭化水素及び水蒸気を導入して $300 \sim 700^\circ\text{C}$ で接触反応させ、同時に反応生成ガス中の水素を該第1の膜を透過させて分離し、反応器に残存した水素及び水蒸気を含む非透過ガスを取り出し冷却して水蒸気を凝縮分離させた後、

このガスから水素を水素選択透過性の第2の膜で分離することを特徴とする水素の製造方法である。

本発明で用いる第1の膜及び第2の膜の材料はPd又はAg, Au, Cu等を含むPd合金が望ましい。これらの膜は水素のみを透過させるため99.99%以上の高純度水素を一挙に得ることができる。純Pd膜の場合、 H_2 存在下では300℃以下で加熱・冷却を繰り返すと膜は H_2 の吸蔵・放出を繰り返すため変形し遂には破壊されやすいが、前記Pd合金膜は300℃付近での低温での H_2 の吸蔵・放出による変形がなく、耐久性に優れており、特に第2の膜として好ましい。

第1の膜及び第2の膜の材料としては、Ni, Coの1種又は2種とVとからなる合金膜の表面にPd又はPd合金を被覆させた水素分離膜（特開平1-262294号公報）でも良い。

更に、第1の膜及び第2の膜の材料としては、多孔質体の表面にPd薄膜を、Pd薄膜上にCu薄膜をそれぞれ化学メッキ法によって形成させ、次

いで加熱処理を行う方法により得られたPd-Cu膜が知られており（特開昭63-294925号公報）、この膜を用いても良い。

Pd合金膜が代表する膜の形状は、反応器が一般に円筒形状であるところから、円筒形が好ましく、場合によっては中空糸繊維状にして多数本束ねた膜モジュールが膜面積の増大と単位面積当たりのガス透過量を増大させることができるところから、更に好ましい。

何れの場合も通常円筒外周側から円筒内部側へ水素が透過するようこれらの膜を用いるのが一般的である。

本発明で使用する水蒸気改質触媒はRh, Ru, Ni, Ir, Pd, Pt, Re, Co, Fe等の金属が担体に担持されたものが一般的である。このうち、特にNi, Ru等を含むものが好ましい。この担体は耐熱性酸化物を含有するのが好ましく、特にアルミナ、マグネシア及び／又は酸化ランタンが適している。これらは触媒金属の耐熱性を向上させると共に、触媒の活性劣化の原因となる炭

7

素析出を抑制する等の効果がある。

本発明における水蒸気改質反応の温度は、高いほど水素生成反応が促進されるが、300~700℃の範囲でよく、従来技術の700~900℃に比較して低い。本発明を550~700℃で実施する場合は従来技術の水蒸気改質触媒を用いても良いが、300~550℃で実施する場合はこれよりも低温活性の優れた触媒を用いる方が良い。この場合は、特に担体たる耐熱性酸化物へのRu, Ni等の触媒金属の分散性を向上させたものが良く、Niは触媒金属中30~90wt%、好ましくは60~80wt%とするのが反応収率上好ましく、一般的に使用されている炭化水素の水蒸気等によるメタン化用触媒は本発明を反応温度300~550℃で実施する際の活性に優れていて適当である。

触媒の製造方法には周知の含漬法、混練法、沈澱法等があり、いずれも適する。

触媒の形状は特に制限はなく、従来知られる球、タブレット、リング等の何れの形状のものでも使用できる。

8

原料である炭化水素としては、ナフサ、LPG、天然ガス、都市ガス等が使用できる。原料中の硫黄は触媒を被毒させるため、硫黄含有原料は触媒を通過する前に脱硫を行うのが良い。

本発明の反応圧力は特に制限はないが、原料側（膜非透過側）圧力が膜透過側圧力より高く、圧力差が大きいほど水素透過速度が大きくなり好ましい。しかし、原料側圧力と膜透過側圧力との圧力差の上限は、膜の強度により制限を受ける。

本発明では、水蒸気改質反応による生成ガス中の水素に第1の膜を透過させた後に、反応器内に残存した水素及び水蒸気を含む非透過ガスを取り出して冷却して水蒸気を凝縮分離してから、これを第2の膜を透過させて分離するが、この第2の膜の材料、形状、ガス透過条件（膜温度、膜非透過側圧力と膜透過側圧力との圧力差等）は第1の膜と同じで良いが、特に膜温度については300~500℃が実用的で好ましい。

第1の膜及び第2の膜の高圧側と低圧側での

9

ガスの流れ形態としては並流型、向流型、交差流型等があるが、特に向流型が好ましい。

第1の膜及び第2の膜と反応器等との接合には溶接式、フランジ式、ねじ込み式、オーリング式等があるが、製品ガスとして純度99.999Vol%以上の高純度水素を目的とする場合は溶接式が良い。

水蒸気改質反応器の加熱器としては通常はバーナーによる火炎燃焼方式を用いるが、触媒燃焼方式でも良い。又、他の高温ガス源を利用するものでもよい。

本発明では多くのプロセス流体を加熱する必要があるが、水蒸気の発生及び原料炭化水素の加熱には水蒸気改質反応器加熱炉からの高温燃焼排ガスを用い、第2の膜に供給するガスについては第2の膜の加熱には、水蒸気改質反応器からの高温の膜非透過ガスを用い、また第2の膜の非透過ガス中には H_2 、 CH_4 、 CO 等の可燃性ガスが残存するので反応器用加熱炉の燃料源とすることにより、熱効率の高い省エネルギープロ

セスとすることができる。

(作用)

本発明では、メタンに代表される炭化水素と水蒸気が水蒸気改質触媒により反応し、反応生成ガス中の水素の1部がPd合金膜で代表される第1の水素選択透過性膜(第1の膜)を透過して高純度で触媒床外に取り出され、反応効率が高められる結果、水素生成量が向上し、反応温度を低下させ得ることから装置材料の耐熱性が緩和され、また触媒活性がより長く維持される。また、上記第1の膜の非透過ガス中の水蒸気を冷却除去した後の水素を含むガスからPd合金膜で代表される第2の水素選択透過性膜から再び高純度水素を取り出し、前記第1の膜を透過させた水素と合流させることにより、水素回収量を増大させることができる。

(実施例)

以下実施例により本発明を具体的に説明するが、本発明はこれらに限定されるものではない。
実施例 1, 2

1 1

以下の実施例は図1に示す試験装置によって実施したので図1を参照しながら説明する。

本発明の製造装置の1例である反応器は、外径2mm、内径1.6mmの先端を閉じたPd合金管を13本束ねた膜18(1本に略記)と、外槽14との間にNi/Al₂O₃系改質触媒16を922g内蔵している。

水蒸気とメタンのモル比(S/C比)を3とした水蒸気・メタン混合ガスが導管10により反応器100に供給される。混合ガスは反応器ヒーター12で加熱され、触媒床16で改質反応を行い、生成水素の1部は膜18を透過して導管20より排出される。

反応生成ガス中の膜非透過ガスは導管22より排出され、冷却器24により水蒸気は凝縮水42となり、気液分離器28より排出される。

水蒸気が除去された反応生成ガスは導管30により膜分離器200に供給される。膜分離器200には膜18と類似のPd合金管から成る膜36が内蔵され、膜温度は膜分離器ヒーター32により400

1 2

℃に保持されている。

反応生成ガス中に残存した水素は膜36を透過して導管38より排出され、導管20より排出された水素とともに導管44に流入し、純度がガスクロマトグラフにより測定され、流量が流量計により測定された後に廃ガス燃焼器で燃焼され、排出された。

膜36の非透過ガスは導管40に排出され、ガスクロマトグラフにより組成分析され、流量が流量計により測定された後に廃ガス燃焼器で燃焼され排出された。

反応温度、膜18及び膜36の膜面積、反応器100での接触時間、水素回収量/供給メタン量を表1に示した。尚、水素回収量とは導管20及び導管38より排出され導管44に流入した水素の合計量である。

又、他の試験条件は下記の通りである。

試験条件：反応圧力 8kg/cm²G

膜透過側圧力 0kg/cm²G

比較例 1, 2, 3

1 3

1 4

比較例として実施例1, 2で用いた膜分離器200を除去し、接触時間と第1の膜の面積を変え、第2の膜を内蔵する膜分離器を使用しないこと以外は全て同じ条件で試験した結果を表1に示した。

比較例4, 5

比較例として実施例で用いた第1の膜の代わりに先端を閉じた金属管を用い、導管20より排出されるガス量をゼロとし、全ての反応生成ガスは、導管22より排出されるようにし、膜2の面積を増大させた以外は全て同じ条件で試験した結果を表1に示した。

15

表 1

条 件	単 位	実 施 例		比 較 例				
		1	2	1	2	3	4	5
反 応 温 度	℃	650	650	650	650	650	650	750
膜 面 積	cm ²							
第1の膜(膜18)		245	245	245	245	300	0	0
第2の膜(膜36)		55	55	0	0	0	300	300
接 触 時 間	sec	29	64	29	64	64	64	64
水素回収量 供給メタン量	mol/mol	1.3	2.4	1.1	2.1	2.2	1.7	1.9

16

4. 図面の簡単な説明

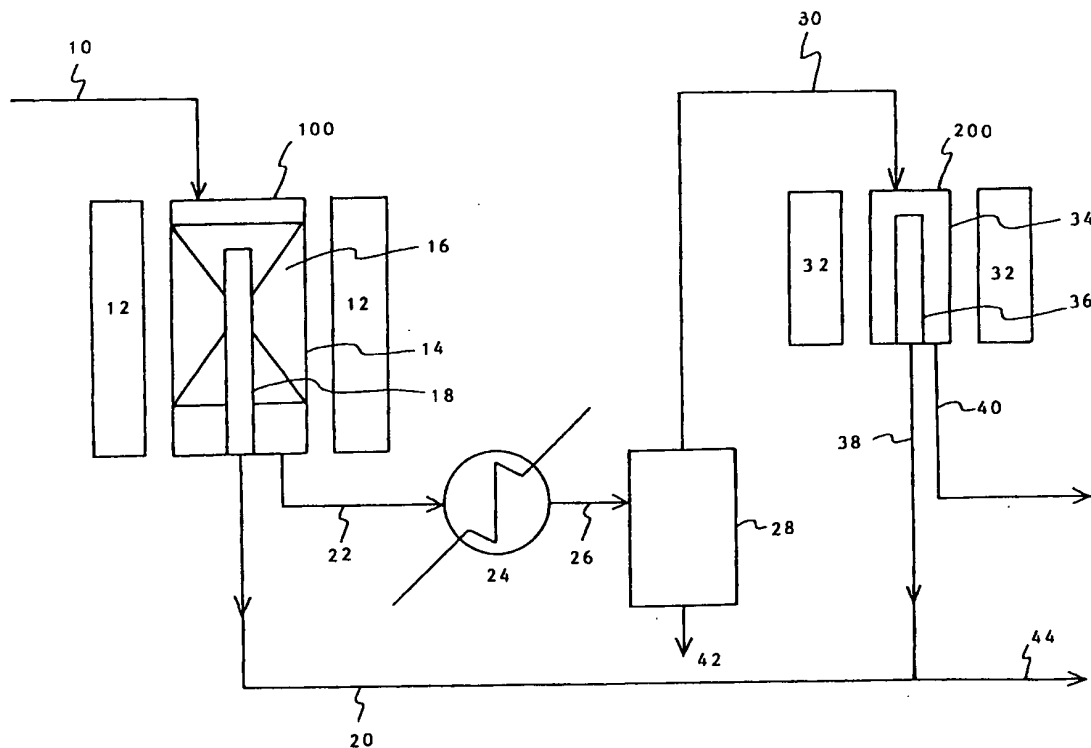
図1は本発明に用いる水素製造装置の一例を示す概略図である。

- 10…原料供給導管
- 16…触媒床
- 18, 36…Pd合金膜
- 20, 38, 44…Pd合金膜透過ガス(高純度水素)
- 出口導管
- 22, 40…Pd合金膜非透過ガス出口導管
- 24…冷却器
- 28…気液分離器
- 42…凝縮水
- 100…反応器
- 200…膜分離器

出願人代理人 古 谷 馨
(外 3 名)

17

図 1



PTO 03-0873

CY=JP DATE=19920629 KIND=A
PN=04-182302

METHOD FOR MANUFACTURING HYDROGEN
[Suiso no seizo hoho]

Shigeo Iiyama, et al.

UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D.C. December 2002

Translated by: FLS, Inc.

PUBLICATION COUNTRY	(10): JP
DOCUMENT NUMBER	(11): 04182302
DOCUMENT KIND	(12): A
PUBLICATION DATE	(43): 19920629
PUBLICATION DATE	(45):
APPLICATION NUMBER	(21): 02310577
APPLICATION DATE	(22): 19901115
ADDITION TO	(61):
INTERNATIONAL CLASSIFICATION	(51): C01B 3/38; B01D 53/22; C01B 3/56
DOMESTIC CLASSIFICATION	(52):
PRIORITY COUNTRY	(33):
PRIORITY NUMBER	(31):
PRIORITY DATE	(32):
INVENTOR	(72): IIYAMA, SHIGEO; SAKAI, NAOHITO.
APPLICANT	(71): PETROLEUM ENERGY CENTER, ETC.
TITLE	(54): METHOD FOR MANUFACTURING HYDROGEN
FOREIGN TITLE	[54A]: SUIISO NO SEIZO HOHO

Specifications

17*

1. Title of the Invention

Method for Manufacturing Hydrogen

2. Claims

1. A method for manufacturing hydrogen characterized by forming a part of a wall from a 1st hydrogen permselective membrane, introducing a hydrocarbon and steam into a reactor packed with a steam reforming catalyst and allowing these to catalyze at 300 to 700°C, simultaneously separating the hydrogen in the reaction-produced gas through said 1st membrane, removing and cooling the impermeable gas containing hydrogen and steam vapor remaining in the reactor, condensing and separating the steam vapor, and subsequently separating the hydrogen from this gas through a 2nd hydrogen permselective membrane.

3. Detailed Specifications

(Field of Industrial Utilization)

The present invention relates to the method for manufacturing hydrogen by subjecting a raw material composed mainly of hydrocarbons, such as naphtha, natural gas, LPG, and municipal gas, to reforming by steam, and in particular, the suitable method for manufacturing high-purity hydrogen with a purity of at least 99.99% which is used in IC applications, such as semiconductor epitaxial and silicon single

*Number in the margin indicates pagination in the foreign text.

crystal usage.

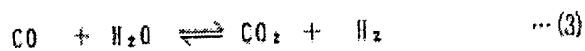
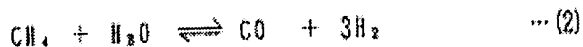
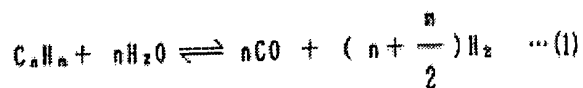
(Problems Which the Invention Intends to Solve)

Methods in which hydrogen is produced by utilizing a steam-reforming reaction on naphtha, natural gas, LPG, and the like are used widely in the industry.

In this method, the raw material hydrocarbon and steam are supplied continuously into a reformer and a gas mixture of H_2 , CO , CO_2 , CH_4 and H_2O is produced by a steam-reforming reaction in a catalytic layer heated to 700 to 900°C, as shown according to the following formulas. This gas mixture is further separated and purified in a CO transformer, decarboxylation device, and methanation device to produce hydrogen gas.

A method in which the above-mentioned gas mixture is cooled, the steam is condensed and separated, and the hydrogen is separated and collected through a hydrogen permselective membrane also is well known.

The hydrocarbon steam-reforming reaction is performed according to the following general formulas (1) to (3).



/8

The reactions in (2) and (3) are reversible. In order to produce a gas high in hydrogen according to the thermodynamic equilibrium in this method, high-temperature conditions are required, but this method has the following problems:

① Since the reactions in formulas (2) and (3) (hereinafter, referred to as "hydrogen-producing reactions") are reversible, the reformed gas is a mixture of H_2 , CO, CO_2 , CH_4 and H_2O . Therefore, in order to produce highly pure H_2 gas, it is necessary to produce that H_2 gas by temporarily removing the reformed gas to outside the system and then separating and purifying it. Namely, it is necessary to provide separation and purification devices in addition to the reformer.

② In order to improve the hydrogen production reactivity in (2) and (3), it is necessary to increase the reaction temperature to $700^\circ C$ to $900^\circ C$ or the steam/hydrocarbon ratio. However, a conversion exceeding the thermodynamic equilibrium value is impossible due to the reversibility of the hydrogen-producing reaction.

③ It is necessary to make the entire device larger, and at the same time, increase the amount of fuel for heating.

④ Resistance to heat at 700 to $900^\circ C$ is demanded of the steam reforming catalyst.

As mentioned above, in order for a high-temperature reaction (700 to $900^\circ C$) to arise using the above-mentioned technique, are larger

reformer and a heat-resistant fuel are required. In addition, the cost of energy rises.

As a method for solving these problems of the above-mentioned technique, there is known a method for manufacturing hydrogen in which part of a wall is formed from a 1st hydrogen permselective membrane, a hydrocarbon and steam are introduced into a reactor packed with a steam reforming catalyst and allowed to catalyze, and simultaneously the hydrogen in the reaction-produced gas is passed through the hydrogen permselective membrane and separated and collected (publication of Tokkai No. 1-219001).

According to this method, the produced hydrogen is removed to outside the reaction system simultaneous to the reaction; hence, the equilibrium shown in the above-mentioned reactions (1) to (3) shifts to the production side, so there are the following advantages:

- ① The hydrogen yield is higher than the thermodynamic equilibrium value,
- ② the reaction temperature can be reduced,
- ③ the separation and purification step can be eliminated after the reaction,
- ④ energy-saving processes are realized through these advantages.

However, this method has the following drawbacks:

- ① Generally in the case of the membrane separation of hydrogen, the bigger the difference in the hydrogen partial pressure on the

membrane-impermeable side and the hydrogen partial pressure on the membrane-permeable side, the higher the amount of hydrogen that permeated through, but 20 to 60% by volume of steam usually remained in the hydrocarbon steam-reforming reaction gas product. The hydrogen partial pressure on the membrane-impermeable side is lower than when no steam is present, and there are limits to the recovery rate (percentage of permeated hydrogen with respect to the amount of hydrogen produced by hydrogen membrane separation).

In order to reduce the amount of steam remaining in the steam-reforming reaction-produced gas, reducing the mole ratio of the steam and raw material hydrocarbon supplied to the reactor also has been considered, but by doing this, carbon easily deposits on the reforming catalyst and the catalytic lifespan is reduced; hence, it is impossible to eliminate the remaining steam in the reforming reaction gas product in a practical manner.

② In order to increase the difference in the hydrogen partial pressure on the membrane-impermeable side and the hydrogen partial pressure on the membrane-permeable side of the steam-reforming reaction-produced gas, a method is known in which the permeable gas side is purged with an inert gas, such as argon gas, to reduce the hydrogen partial pressure on the permeable side, but in this case, argon gas or the like becomes mixed with the hydrogen product, which causes the impurity concentration to increase.

The object of the present invention is to obtain a method for manufacturing hydrogen which gives a higher hydrogen recovery rate than in the aforesaid prior art during the manufacture of hydrogen by steam reforming of a raw material composed mainly of a hydrocarbon.
(Means Used to Solve the Problems)

Namely, the present invention is a method for manufacturing hydrogen characterized by forming a part of a wall from a 1st hydrogen permselective membrane, introducing a hydrocarbon and steam into a reactor packed with a steam reforming catalyst and allowing these to catalyze at 300 to 700°C, simultaneously separating the hydrogen in the reaction gas product through said 1st membrane, removing and cooling the impermeable gas containing hydrogen and steam vapor remaining in the reactor, condensing and separating the steam vapor, and subsequently separating the hydrogen from this gas through a 2nd hydrogen permselective membrane. /9

Pd or a Pd alloy containing Ag, Au, Cu and the like is desirable for the raw material of the 1st and 2nd membranes used in the present invention. In order for hydrogen only to permeate through these membranes, a high-purity hydrogen of at least 99.99% can be obtained in one fell swoop. In the case of a pure Pd membrane, by repeating heating and cooling at 300°C or less in the presence of H₂, the membrane deforms because the H₂ is repeatedly occluded and discharged and thus easily destroyed, but the aforesaid Pd alloy membrane is not

deformed by occlusion and discharge of H_2 at a low temperature close to $300^\circ C$ and it has outstanding durability, so it is especially preferable as the 2nd membrane.

The material of the 1st and 2nd membranes may be a hydrogen separation membrane in which the surface of an alloy membrane comprising one or more of Ni and Co as well as V is covered with Pd or a Pd alloy (publication of Tokkai No. 1-262294).

Furthermore, a Pd-Cu membrane obtained in a method in which a Pd thin film is formed on the surface a porous body and a Cu thin film is formed on the Pd thin film in respective chemical plating methods and then a heat treatment is performed is known (publication of Tokkai No. 63-294925) and can be used for the material of the 1st and 2nd membranes.

The shape of a typical Pd alloy membrane in a reactor is generally cylindrical; hence, a cylindrical shape is preferable. Depending on the situation, numerous membrane modules bundled into the shape of hollow fibers are more preferable because the membrane surface area is large and the amount of gas permeating through them can be increased per unit surface area.

In either case, these membranes are generally used so that the hydrogen will usually permeate through to the interior of the cylinder from outside of the cylinder.

The steam reforming catalyst used in the present invention is generally one carried on a carrier which is a metal, such as Rh, Ru, Ni, Ir, Pd, Pt, Re, Co or Fe. Out of these metals, Ni, Ru and the like are more preferably contained. It is preferable that this carrier contain a heat-resistant oxide, and alumina, magnesia and/or tantalum oxide are especially suitable. These oxides improve the heat resistance of the catalyst metal, and at the same time, there are advantages because carbon deposition, which is the cause of deterioration of the activity of the catalyst, is inhibited, among other advantages.

The higher the temperature of the steam-reforming reaction in the present invention, the faster the hydrogen-producing reaction proceeds, but it should range from 300 to 700°C, which is lower than the temperature of 700 to 900°C in the prior art. When the present invention is carried out at 550 to 700°C, the steam reforming catalyst in the prior art can be used, but when it is carried out at 300 to 550°C, it is better to use a catalyst with more outstanding low-temperature activity. In this case, the dispersibility of the catalytic metal, such as Ru or Ni, in the heat-resistant oxide serving as the carrier should be improved. It is preferable from the standpoint of reaction yield that there be 30 to 90% by weight, and more preferably, 60 to 80% by weight of Ni in the catalyst metal. The catalyst for methanation utilizing a hydrocarbon, steam, and the like

that is generally used is ideal because it is outstanding in activity while carrying out the present invention at a reaction temperature of 300 to 550°C.

There are well-known impregnation/immersion, mixing/kneading and precipitation methods, among other methods for the method for manufacturing the catalyst. Any of these methods are suitable.

The shape of the catalyst is not limited and any conventionally known shape, such as a sphere, table, ring, or the like can be used.

Naphtha, LPG, natural gas, municipal gas, and the like can be used for the raw material hydrocarbon. The sulfur in the raw material is a catalyst poison; hence, desulfurization should be performed on sulfur-containing raw materials before passing through the catalyst.

The reaction pressure of the present invention is not particularly limited, but the pressure on the raw material side (membrane-impermeable side) is preferably higher than the pressure on the membrane-permeable side, so the larger the pressure difference, the faster the hydrogen permeation speed is. However, the upper limits of the difference in the pressure on the raw material side and the pressure on the membrane permeation side is suppressed by the membrane strength.

In the present invention, the hydrogen in the gas produced by the steam-reforming reaction passes through the 1st membrane, the impermeable gas containing the hydrogen and steam remaining in the

reactor is removed and cooled to condense and separate the steam, after which it is separated by passing it through the 2nd membrane. However, the material, shape and gas permeation conditions (the membrane temperature, difference in the pressure on the membrane-impermeable side and the pressure on the membrane-permeable side, etc.) of this 2nd membrane may be the same as those for the 1st membrane, but 300 to 500°C is especially preferable for the membrane temperature for practical use.

The form of the gas stream between the high- pressure and low-pressure sides of the 1st and 2nd membranes can be a parallel, counter, or cross stream, and the like, but a counter flow is more preferable. /10

The 1st and 2nd membrane reactor can be a welding, flange, screwing-in or o-ring type one, and the like, but the reactor can be a welding-type reactor when a high-purity hydrogen having a 99.999% by volume purity is the target gas product.

A flame combustion system making use of burners is usually used for the heater of the steam reforming reactor, but it may be a catalytic combustion system. Or, another high-temperature gas source can be used.

It is necessary to heat a large quantity of process fluid in the present invention, but a high-temperature combustion waste gas from a steam reforming reactor heating furnace can be used for producing

steam and heating the raw material hydrocarbons, a high-temperature membrane-impermeable gas from the steam reforming reactor can be used for heating the gas passing through the 2nd membrane and thus the 2nd membrane, and a combustible gas containing H₂, CH₄, CO, and the like remains in the 2nd membrane-impermeable gas; hence, by making the fuel source from the heating furnace, an energy-saving process with a high heat efficiency can be obtained.

(Operation)

As a result of the hydrocarbon, represented by methane, and the steam reacting using the steam reforming catalyst in the present invention, part of the hydrogen in the reaction gas product passing through the 1st hydrogen permselective membrane (1st membrane), represented by a Pd alloy membrane, high-purity hydrogen being removed to outside the catalytic bed, and the reaction efficiency increasing, the amount of hydrogen produced can be increased and the reaction temperature can be reduced; hence, the heat resistance of the material constituting the device is improved fully and the catalytic activity is maintained longer. Moreover, by cooling and removing the steam in the above-mentioned 1st membrane-impermeable gas, subsequently removing the high-purity hydrogen again through the 2nd hydrogen permselective membrane, which is represented by a Pd alloy membrane, and merging it with the hydrogen that passed through the aforesaid 1st membrane, the amount of the hydrogen recovered can be increased.

(Practical Examples)

The present invention will now be explained specifically through the practical examples, but the present invention is not limited to them.

Practical Examples 1 and 2

The following practical examples were carried out using the test device shown in Figure 1; hence, they will be explained while referring to Figure 1.

The reactor, which is an example of the manufacturing device of the present invention, is packed with 922 g of an Ni/Al₂O₃-based reforming catalyst **16** between membranes **18** (abbreviated to one membrane) bundled from thirteen 2 mm OD and 1.6 mm ID Pd alloy tubes whose leading ends were occluded, and an outer tank **14**.

A steam/methane gas mixture whose steam/methane mole ratio (S/C ratio) is 3 is supplied to a reactor **100** through a duct **10**. The gas mixture is heated by a reactor heater **12** and a reforming reaction is performed in a catalytic bed **16**. Part of the produced hydrogen passes through the membrane **18** and discharged through a duct **20**.

The membrane-impermeable gas in the reaction-produced gas is discharged through a duct **22** and the steam is turned into condensed water **42** by a cooler **24**, and discharged through a gas-liquid separator **28**.

The reaction gas product from which the steam has been removed is supplied to a membrane separator **200** through a duct **30**. The membrane separator **200** is packed with a membrane **36** comprising Pd alloy tubes similar to the membrane **18**, and the membrane temperature is held at 400°C by using a membrane separator heater **32**.

The hydrogen remaining in the reaction-produced gas passes through the membrane **36**, is discharged through a duct **38**, flows in through a duct **44** along with the hydrogen discharged through the duct **20**, the purity is measured by gas chromatography and the flow rate is measured with a flowmeter, after which it is combusted by a waste gas burner and discharged.

The membrane **36**-impermeable gas is discharged through a duct **40**, its composition is analyzed by gas chromatography, the flow rate is measured by a flowmeter, and it is subsequently combusted by a waste gas burner and discharged.

The reaction temperature, surface area of the membrane **18** and membrane **36**, contact time of the reactor **100**, and the amounts of hydrogen recovered and methane supplied have been shown in Table 1. Moreover, the amount of the hydrogen recovered is the total amount of the hydrogen discharged through the duct **20** and duct **38** and the hydrogen flowing in through the duct **44**.

The other test conditions are as follows:

Test conditions:

Reaction pressure 8 kg/cm²G
Pressure on membrane-permeable side 0 kg/cm²G

Comparative Examples 1, 2 and 3

Except for removing the membrane separator **200** used in /11
Practical Examples 1 and 2, changing the contact time and the surface
area of the 1st membrane, and not using the membrane separator packed
with the 2nd membrane, the test results at all the same conditions
have been shown in Table 1 as these comparative examples.

Comparative Examples 4 and 5

Except for using metal tube occluded at the leading end instead
of the 1st membrane used in the practical examples, making the amount
of gas discharged through the duct **20** zero, and increasing the surface
area of the 2nd membrane so that all of the reaction-produced gas is
discharged through the duct **22**, the test results at all the same
conditions have been shown in Table 1.

Table 1

Conditions	Unit	Practical Examples		Comparative Examples				
		1	2	1	2	3	4	5
Reaction Temperature	°C	650	650	650	650	650	650	750
Membrane Surface Area	cm ²							
1st Membrane (Membrane 18)		245	245	245	245	300	0	0
2nd Membrane (Membrane 36)		55	55	0	0	0	300	300
Contact Time	sec	29	64	29	64	64	64	64
Hydrogen Recovery Rate Amount of Methane Supplied	mol/mol	1.3	2.4	1.1	2.1	2.2	1.7	1.9

4. Brief Description of the Figures

/12

Figure 1 is a schematic diagram showing an example of the device for producing hydrogen used in the present invention.

10: duct for supplying raw material(s); 16: catalytic bed; 18, 36: Pd alloy membranes; 20, 38, 44: Pd alloy membrane-permeable gas (high-purity hydrogen) discharge ducts; 22, 40: Pd alloy membrane-impermeable gas discharge ducts; 24: cooler; 28: gas-liquid separator; 42: condensed water; 100: reactor; 200: membrane separator

Figure 1

